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Atmospheric
Chemistry
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Discussions

Interactive comment on "Detection of regional scale sea-to-air oxygen emission related to spring bloom near Japan by using in-situ measurements of atmospheric oxygen/nitrogen ratio" *by* H. Yamagishi et al.

H. Yamagishi et al.

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Author Comments to Referee No. 2

We thank for valuable and constructive comments, to which we reply in the following:

» *Most of the sampling and measurement procedure is discussed in great detail. When it comes to the actual measurement I am missing some information. The -80°C coldtrap will fill up with time. What is the procedure to condition this trap? From the sketch I see that there are four traps. How is that working?*« We added an explanation in section 2.1 of the revised manuscript about how the cold traps work. We also added some practical information that is useful for long term monitoring, for example the material of a rotor in a Valco(R) valve, in section 2.1.

»*I understand that a column is used to separate* N_2 *from* O_2*/Ar. What type of column is that? If it is a 5A is accumulation of* CO_2 *a problem? I could not find how big your sample loop is. Also are you alternating sample and standard or do you do less standards than samples?*« We added a brief introduction of the GC/TCD method for the O_2/N_2 ratio measurement in section 2.1 to specify referee's questions. Accumulation of CO_2 seems not to be a problem for the O_2/N_2 ratio measurements. We add the following sentence in section 2.1: ”Although CO_2 will be trapped in the MS-5A column, the accumulation of CO_2 is unlikely to affect the O_2/N_2 ratio measurement within a month.” We also added a sentence about the maintenance of the separation column in section 2.2: ”The separation column is baked at 320°C for 300 minutes and the vapor traps (both the 80-mL glass traps and the 1/8” OD nickel tubing traps) are dried.”

»*A figure with your detector signals might be interesting. How long do you need for one measurement?*« Since a figure of the detector signals will be the same as Figure 1 of Tohjima (2000), we think that a few sentences are enough for an explanation in this paper. So we replace the sentence of p.2231 lines 10-12 in section 2.3 (Data processing) to the following sentence: ”The ratio of the (O_2+Ar) peak area to the N_2 peak area is directly determined from the peak areas of a (O_2+Ar) peak and a N_2 peak of the GC/TCD signal (as shown in Figure 1 of Tohjima, 2000).” We added additional useful technical information about processing chromatogram to compute peak areas in the next sentences in the revised manuscript.

»*page 2232, line 5: delete ”relatively”*« We deleted ”relatively” and replaced the sentence to the following: ”This is a valid assumption, since changes in the Ar/N_2 ratio”.

»*page 2234, line 26..: I doubt that the back pressure regulator is causing the offset between flasks and in-situ measurements. At this high flow rate any fractionation at the back pressure regulator can not diffuse back to the sample intake unless there*

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is a lot of turbulence.« We recently found that the back pressure regulator is not the cause of the bias and added new results in the revised manuscript. Thus, we deleted some discussions about the fractionation at the back pressure regulator. We added the following sentences in section 3.1: ”We added a 6 mm OD, 4 m long Dekabon(R) tubing coil between the spherical glass flask and the back pressure regulator on 22 August 2007. However, the bias still remains at the same extent after the installation of the long tubing coil (data are not shown). The Teflon cock attached on the spherical glass flask may cause a small leaking to fractionate O_2 and N_2 and then accumulate O_2 in the spherical flask.” We now doubt a small leaking at the Teflon cock on the spherical glass flask. But we have not identified the cause of the bias yet.

»*page 2235, section 3.2: The observation of higher variability in the O_2 /N_2 ratio than in the APO is not obvious to me. Can you quantify this observation?*« We quantified the difference of the standard deviation of the residuals of the O_2/N_2 ratio and APO, which were computed after subtraction of the best fit curve from the one-day averaged observational data. We added sentences in section 3.2 to reflect this: ”Negative spikes of the O_2/N_2 ratio accompanied by positive CO_2 spikes were observed especially between August and October (Fig. 2a). Monthly averaged standard deviations of anomaly O_2 /N_2 ratio are 32.1, 18.3, and 16.0 for August, September, and October, respectively (n = 29, 28, 30, respectively), whereas monthly averaged standard deviations of anomaly APO are 13.2, 3.3, and 2.2, respectively (n = 29, 26, 30, respectively), where anomaly O_2/N_2 ratio and APO are daily averaged residuals that were de-trended and de-seasonalized from the observational data following Tohjima et al. (2008). The higher variability in the O_2/N_2 ratios, relative to the APO variability, should be attributed to terrestrial processes such as respiration of terrestrial biosphere and fossil fuel combustion.”

»*Also I do not understand why this is supporting a terrestrial source.* « In this paper, our intent has been to focus on the ocean processes. So we did not include discussion about the O_2:C exchange ratio to separate out the contributions of terrestrial biosphere

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and fossil fuel combustion. We replaced the phrase of ”terrestrial biosphere” in p.2235 line 27 to ”terrestrial processes such as respiration of terrestrial biosphere and fossil fuel combustion”.

»*Are you not explaining the fast* O_2 *changes with oceanic sources later on in the paper.*« We added an order of magnitude estimation in the revised manuscript to verify if the APO variabilities can be attributed to the sea-to-air oxygen flux. Simple estimation indicated that the variation of APO seems to be consistent with the oxygen emission due to active primary production of the regional-scale bloom.

References

Tohjima, Y.: Method for measuring changes in the atmospheric O_2/N_2 ratio by a gas chromatograph equipped with a thermal conductivity detector, J. Geophys. Res.-Atmos., 105(D11), 14575-14584, 2000.

Tohjima, Y., Mukai, H., Nojiri, Y., Yamagishi, H., and Machida, T.: Atmospheric O_2/N_2 measurements at two Japanese sites: estimation of global oceanic and land biotic carbon sinks and analysis of the variations in atmospheric potential oxygen (APO), Tellus Series B-Chemical and Physical Meteorology, 60(2), 213-225, doi: 10.1111/J.1600-0889.2007.00334.X, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2225, 2008.